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Description

The present invention relates to a method of reducing the spot formation and the drying time in machine dishwashing operations.

5 In the mechanical washing of dishes, the articles to be cleaned generally are first subjected to a main washing step, which is subsequently followed by one or more rinsing steps to remove adhering main-wash detergent ingredients or remaining soil.

It is customary to add in the rinsing step a rinse aid which causes the article to dry more evenly and improves the visual appearance thereof when dry.

10 Despite the use of such rinse aids, the visual appearance of articles after the mechanical washing process often is still not optimal, owing to spot formation during the drying process.

It has been proposed in European Patent Application No 0 139 330 to reduce the formation of spots on the rinsed articles by using a rinse aid which includes a limited amount of a layered clay.

15 It has now been found that a significant reduction of spot formations during the drying process is also achieved by inclusion of colloids such as colloidal silica or alumina in the rinse-aid composition.

It has further been found that the use in the rinse aid of colloids having non-plate-shaped particles such as colloidal silica or alumina gives a surprising reduction in the drying time of the rinsed articles.

Reduction of the drying time is of the utmost relevance to machine dishwashing operations, particularly in industrial, semi-industrial or institutional machine dishwashing applications.

20 The reduction of the drying time and the fact that, by inclusion of colloids of the above type, the conventional nonionic surfactant component can be deleted, opens the possibility of reducing the temperature in the rinsing cycle and consequently achieving energy savings, without being confronted with an over-foam problem (due to reduction of the temperature to below the cloud point of the nonionic surfactant).

Inclusion of colloidal silica in fully formulated liquid detergent compositions is well known.

25 In EP-A-0 110 472 the use of silica as a corrosion-inhibiting agent in aqueous liquid detergent compositions is described.

In US-A-3 354 088 amorphous silica is used as a flow-retarding agent in an aqueous aerosol-type window cleaner.

In DE-A-3.439.872 amorphous silica is used as an abrasive in aqueous liquid detergent compositions.

30 In US-A-3 736 259 and US-A-3 919 101 the use of silica in carpet-cleaning compositions is described.

Finally in US-A-3 037 888 aqueous liquids containing colloidal silicas for use in metal cleaning are described.

To our knowledge, the inclusion in rinse-aid products of a non-plate-shaped colloid such as colloidal silica or alumina as an anti-spotting agent or as an agent for reducing drying time has never been described 35 or suggested.

Accordingly, the present invention provides a method of reducing the spot formation and the drying time in machine dishwashing operations, comprising the addition of a non-plate-shaped colloid to the liquor for rinsing the dishes.

40 For the purposes of the present invention, the term "non-plate-shaped colloid" encompasses all colloids having a particle shape which is not characterised by a size in one dimension which is significantly smaller than the sizes in the other two dimensions.

In particular, colloids having approximately spherical particles are preferred, suitable examples of which are the colloidal forms of silica alumina and titania.

45 The colloid suitable for use in the method of the present invention preferably has a relatively low average elementary particle size typical for colloidal solution-forming particles, ranging from 0.001 to 1 micrometre, or even 5 micrometres. The lower portion of this range, particularly the range of 0.002 to 0.05 micrometres, is preferred for reasons of effectiveness.

The most preferred type of colloid for use in accordance with the present invention is colloidal silica.

50 A range of suitable silicas is commercially available under the trade name Ludox colloidal silica in various grades (Ludox is a Registered Trade Mark of the Du Pont Company), under the trade name Syton colloidal silica (Syton is a Registered Trade Mark of the Monsanto Company) and in various grades under the trade name Aerosil (Aerosil is a Registered Trade Mark of Degussa). Ludox is a precipitated silica, whilst Aerosil is a flame hydrolysed silica.

55 The colloid may be added to the rinsing liquor as such, or it may be added in the form of a colloidal dispersion or in the form of a rinse-aid composition in any suitable physical form comprising the colloid and further suitable conventional rinse-aid ingredients.

The level of the colloid in the rinsing liquor should be such that the rinsing liquor contains from 0.5 to 150 mg of the colloid per litre.

Rinse-aid compositions for use in accordance with the present invention may include the colloid in an amount of from 0.2 to 25% by weight. An amount of from 0.5 to 10% is preferred, an amount of 1 to 5% by weight being preferred most.

Suitable rinse-aid compositions may optionally comprise an acidic compound, in particular an organic acid, such as eg citric, adipic, glutaric or succinic acid. The acidic compound may be included in an amount of up to 50% by weight, preferably from 5 to 30% by weight.

However, it has surprisingly been found that the reduction in spotting brought about by the addition of, eg citric acid to conventional rinse aid formulations is equalled by the use of the colloid-containing rinse aids of the present invention when citric acid is absent. The ability to omit such organic acids whilst achieving comparable effects provides considerable economic advantages.

Further suitable conventional ingredients for inclusion in the compositions for use according to the present invention are hydrotropic agents such as butylated hydroxytoluene, alcohols, wetting agents such as nonionic surfactants, perfumes, germicides, anti-corrosion agents and colouring agents.

The addition of short-chain, water-soluble alcohols (eg C₁-C₃) to the rinse aid according to the present invention is particularly preferred. It has been found that the colloidal sol may form a precipitate in conjunction with some conventional rinse-aids. This may occur, eg on refilling the rinse-aid dispenser with rinse-aid, a residue of the previous, different rinse-aid often remaining. Alcohol may be included in an amount up to 40%, preferably 10-30% by weight, most preferably 20-30% by weight.

The rinse-aid may be used in conjunction with all conventional main-wash products, both enzymic and non-enzymatic. Such products may be in any known form, eg powders, liquids or tablets.

It will be understood that the rinse-aid may contain two-dimensional aggregated arrays of the non-plate-shaped colloid. Processes for the preparation of such aggregates have been described within US Patent 2 801 902 and EP-A-246757, published on 25.11.87. Such arrays are usually in the form of compact monolayers. The most preferred colloid demonstrating this behaviour is silica sol.

The invention will be further illustrated by way of examples.

Examples

In the experiments described in the examples below, a standard set of glassware soiled with a standard evaluation soil was used to evaluate spot and film formation.

The experiments were carried out in the following commercially-available dishwashing machines:

- (1) Miele G 560, sold by Miele & Cie, Germany;
- (2) Zanussi Z 82, sold by Industrie Zanussi SpA, Italy;
- (3) Bosch M 500, sold by Bosch-Siemens Hausgeräte GmbH, Germany.

In the washing programmes, tap water of about 9 degrees German hardness was used and machine dishwashing main-wash products having a composition as indicated below were dosed at a product concentration of 3 g/l. The rinse-aid products, if any, were added to the final rinsing liquor at a dosage of 3 ml per rinse (approximately 10 litres).

Main-wash Product Compositions:				
Ingredients	A	B	C	D
Sodium tripolyphosphate	33	33	33	36
Sodium metasilicate	-	50	33	17
Sodium disilicate	9	-	-	-
Sodium carbonate	9	-	-	-
Amylase	1.8	-	0.5	0.6
Protease	1.8	-	1.0	0.6
Tetraacetylenediamine	3.6	-	-	-
Sodium perborate.4 aq.	8	-	10	9
Calcium salt of ethylenediaminetetraphosphonic acid	0.6	-	-	-
Alkoxylated nonionic surfactant	-	1.0	1.5	-
Potassium salt of dichlorocyanuric acid	-	2.1	-	-
Sodium sulphate/water	-----balance -----			

After the main-wash and rinse steps, the glassware, when dry, was visually assessed as to spot and film formation using the following scales:

- 1 = no spots
 2 = 1-5 spots
 3 = 6-10 spots
 4 = 11-20 spots
 5 = more than 20 spots
- 1 = no film formation
 2 = traces of film formation
 3 = moderate film formation
 4 = heavy film formation

Example 1

The spot and film formation effects of the addition of a series of rinse-aid products simply consisting of aqueous dispersions of colloidal silica were measured at various concentrations of the colloidal silica.

All experiments were carried out in dishwashing machine type (1), using main-wash product type A, at two temperatures of the final rinse.

The following results were obtained:

<u>Final rinse temperature</u>		<u>65°C</u>	<u>45°C</u>	<u>65°C</u>	<u>45°C</u>
<u>Rinse aid</u>		<u>Spot</u>		<u>Film</u>	
No rinse aid		4.4	3.9	1.1	1.4
5 % Ludox SM (1)		3.2	2.7	2.1	2.1
6 % Ludox TM (2)		1.8	1.9	2.1	2.1
7.5% Ludox SM		2.1	2.4	2.0	2.1
10 % Ludox SM		1.7	2.0	2.2	2.0
10 % Ludox AM (3)		2.4	2.4	2.0	2.0
16 % Ludox SM		1.4	-	2.6	-

(1) Ludox SM (RTM) is a colloidal silica (30% by weight as SiO_2 ; counter-ion is sodium) ex Du Pont, having an average particle size of 7 nm.

(2) Ludox TM (RTM) is a colloidal silica (50% by weight as SiO_2 ; counter-ion is sodium) ex Du Pont, having an average particle size of 22 nm.

(3) Ludox AM (RTM) is a colloidal silica (30% by weight as SiO_2 ; counter-ion is sodium) ex Du Pont, having an average particle size of 12 nm.

Example 2

In a dishwashing machine of type (2), using a main-wash product type B, the spot- and film-forming behaviour of a rinse-aid composition in accordance with the present invention was measured after 1 and 4 programme cycles at final rinse temperatures of 40 and 60 °C. The composition of the rinse aid was as follows:

Ingredients	% by weight
Ludox SM	7.5
Citric acid	18.0
Butylhydroxytoluene	0.1
Colouring agent	0.003
Water	balance

The following results were obtained:

<u>Final rinse temperature</u>	<u>60 °C</u>	<u>40 °C</u>	<u>60 °C</u>	<u>40 °C</u>
<u>After 1 wash cycle</u>	<u>Spot</u>		<u>Film</u>	
Without rinse aid	2.9	4.0	2.0	2.0
With rinse aid	2.0	1.0	2.0	2.0
<u>After 4 wash cycles</u>	<u>Spot</u>		<u>Film</u>	
Without rinse aid	4.0	4.0	2.0	2.0
With rinse aid	2.0	2.0	2.0	2.0

Example 3

Using dishwashing machine type (3) and main-wash products C and D, the spot and film formation behaviour of the rinse-aid composition used in Example 2 was assessed at 55 °C final rinse temperature.

The following results were obtained:

Main-wash product	C	D	C	D
	Spot		Film	
Without rinse aid	3.9	4.8	1.5	1.4
With rinse aid	1.9	2.0	2.0	2.0

Example 4

The drying times after the final rinse of a standard set of glassware were measured in an industrial Electrolux D48 single-tank washing machine sold by Electrolux-Wascator, Sweden, using the normal washing programme at 60 °C, and tap water of 8 degrees German hardness.

A comparison was made between final rinses with three conventional rinse aids and the rinse aid of Example 2.

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The compositions of the conventional rinse-aid products were as follows:

	Ingredients	1	2	3
5	Alkoxylated nonionic surfactants	10.0	50.0	-
	Layered clay	-	-	8.0
	Citric acid	18.0	-	-
	Formaline	-	0.1	-
	Sodium xylene sulphonate	3.0	-	-
10	Butylhydroxytoluene	0.1	-	-
	Colouring agent	0.003	0.003	-
	Water	-----balance -----		

15 The rinse aids were added at a concentration of 0.2 g/l.
 Experiments were carried out at three temperatures of the final rinse.
 Drying times are expressed as a drying time range since they are dependent upon the heat capacity
 and consequently the thickness of the individual glass articles.
 The following results were obtained:

		Drying Time in Seconds		
	Final rinse temperature	60 ° C	70 ° C	80 ° C
25	Conventional rinse aid 1	61-160	55-137	43-95
	Conventional rinse aid 2	57-170	53-169	43-125
	Conventional rinse aid 3	59-177		
	Rinse aid according to Example 2	43-71	45-60	31-43

30 Example 5

In a set of comparative experiments analogous to Example 4, the foam behaviour of the various rinse
 aids was measured. The foam behaviour is expressed in cm of foam above the wash bath.

35 The following results were obtained:

		cm of Foam Above Wash Bath				
	Final rinse temperature	30 ° C	40 ° C	50 ° C	60 ° C	70 ° C
40	Conventional rinse aid 1	5	5	3	1	1
	Conventional rinse aid 2	3	3	3	2	1
	Conventional rinse aid 3	0	1	1	2	1
	Rinse aid according to Example 2	2	1	1	0	0

45 Example 6

In further comparative experiments, the influence of type of rinse aid on glass appearance was tested.
 50 Comparisons were made in machine type (3) after 1 and 4 wash cycles with main-wash product A, the final
 rinse temperature being 65 ° C.

The following results were obtained:

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Number of cycles	1	4	1	4
	Spot		Film	
Without rinse aid	4.7	4.7	1.5	1.5
Ludox SM (0% citric acid)	1.5	1.5	2.4	2.4
Conventional Product 1	3.5	3.5	2.3	2.5

Example 7

An experiment was carried out to determine the stability of a rinse aid according to the present invention in admixture with a conventionally used rinse-aid (Product 1). This experiment demonstrates stability as a new rinse-aid is added to the dispenser before the old rinse-aid has been exhausted. Negligible (<5%) flocculation occurs if 25 wt % iso-propanol is added to a Ludox-based rinse-aid when the dispenser is at least one-third exhausted of conventional rinse-aid.

Conventional Product: Ludox Rinse Aid	Flocculation
90:10	5%
75:25	approx 30%
66:33	5%
50:50	<5%
25:75	<5%
10:90	approx 0%

Example 8

Using dishwashing machine type (1) and main-wash product type B, the spot and film formation behaviour of a Ludox SM rinse-aid with varying amounts of citric acid was assessed at 65°C final rinse temperature with 260 French hard water. A build-up of 4 wash cycles was assessed.

0% Citric 6% Citric 12% Citric 18% Citric None

Tumbler

Spot	2.3	2.1	2.1	3.1	3.0
Film	4.0	4.0	4.0	3.5	2.7

Cutlery

Spot	1.9	1.7	1.5	1.9	3.0
Film	2.1	2.1	2.0	2.2	3.0

Example 7

The spot and film formation effects of Ludox-based rinse-aids with and without citrate were assessed, using dishwashing machine type (1) and main-wash product type C. Final rinse temperature was 40°C or 60°C. Assessment was made after 1 and 4 wash cycles. Comparison with conventional product 1 was made.

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	<u>40°C</u>	<u>None</u>		<u>+0%</u> <u>Citrate</u>		<u>+18%</u> <u>Citrate</u>		<u>1</u>	
5		<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>
10	Spots								
	Tumbler	2.1	2.7	2.0	2.0	1.7	2.3	1.1	1.5
	Film								
15	Tumbler	3.0	3.0	3.0	3.8	3.0	3.5	3.0	3.6
	Spots								
20	Knives	2.4	2.4	1.3	1.4	1.7	1.5	2.6	3.4
	Film								
25	Knives	2.4	2.7	2.3	2.5	2.4	2.5	2.7	2.9
30	<u>60°C</u>	<u>None</u>		<u>+0%</u> <u>Citrate</u>		<u>+18%</u> <u>Citrate</u>		<u>1</u>	
		<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>	<u>1</u>	<u>4</u>
35	Spots								
	Tumbler	1.9	3.4	1.5	1.5	1.9	2.0	2.0	1.6
40	Film								
	Tumbler	3.0	3.0	3.0	4.0	3.0	3.5	4.0	4.0
45	Spots								
	Knives	2.2	2.4	1.3	1.3	1.5	1.4	1.6	2.4
50	Film								
	Knives	2.6	2.9	2.8	2.6	2.6	2.3	2.8	2.8

Example 10

A number of colloids were tested for their rinse-aid benefit. Main-wash at 60°C using 2 g/l of main-wash

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product B was followed by rinse at 65 ° C. The dosage of colloids was assessed by total surface area.

Type of Colloid	Surface Area (M ²)	Spot	Film
Alumina C	22.5	4.6	1.6
	60	2.0	2.6
	75	2.0	2.3
	100	2.1	2.3
Lepandin® 20 N	20	4.8	1.5
	60	2.0	2.2
	75	1.8	2.2
	100	1.8	2.2
TiO ₂	25	3.7	1.9
	50	4.6	3.1
	75	2.8	3.7
	100	1.6	3.7
Dispersal®	50	2.2	2.0
	75	2.4	2.1
	100	1.8	2.0
Ludox® SM	27	1.6	2.2
	81	1.5	2.1
	100	1.5	2.0
Aerosil® 380	30	2.4	2.1
	90	1.2	2.8
	120	1.5	2.7
Blank	-	4.0	1.4

Lepandin and Aerosil are products of Degussa. The former is an alumina, the latter a silica. Dispersal is a product of Condea, and is an alumina. Ludox SM is a product of Du Pont, and is a silica.

Claims

1. A method of reducing the spot formation and the drying time in machine dishwashing operations, characterized by the addition of a non-plate-shaped colloid to the rinse liquor in an amount of from 0.5 to 150 mg of colloid per litre rinse.
2. A method according to claim 1, characterized in that the non-plate-shaped colloid is a silica, alumina or titania.
3. A method according to claim 1 or 2, characterized in that the colloid has a particle size ranging from 0.001 to 1 micrometer.
4. A method according to claim 1, 2 or 3, characterized in that the colloid is added as two-dimensional array of particles.

Revendications

1. Une méthode pour réduire la formation de tâches ainsi que le temps de séchage dans les étapes de fonctionnement des machines à laver la vaisselle, caractérisée par l'addition d'un colloïde non conformé en plaquettes à la liqueur de rinçage en une quantité de 0,5 à 150 mg de colloïde par litre de rinçage.
2. Une méthode selon la revendication 1, caractérisée en ce que le colloïde non conformé en plaquettes est de la silice, de l'alumine ou de l'oxyde de titane.

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3. Une méthode selon la revendication 1 ou 2, caractérisée en ce que le colloïde présente une dimension des particules dans la gamme de 0,001 à 1 micron.
4. Une méthode selon la revendication 1, 2 ou 3, caractérisée en ce que le colloïde est ajouté sous la
5 forme d'une rangée bidimensionnelle de particules.

Patentansprüche

1. Verfahren zur Verringerung der Fleckenbildung und Trocknungszeit bei Geschirrspülmaschinenvorgängen, gekennzeichnet durch die Zufügung eines nicht-plattenförmigen Kolloids zu der Spülflüssigkeit in
10 einer Menge von 0,5 bis 150 mg Kolloid pro Liter Spülwasser.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das nicht-plattenförmige Kolloid eine Kiese-
15 lerde, Aluminiumoxid oder Titandioxid ist.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Kolloid eine Teilchengröße im
Bereich von 0,001 bis 1 Mikrometer aufweist.
4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, daß das Kolloid als zweidimensionale
20 Anordnung von Teilchen zugefügt wird.

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